

CONTROL OF HEAVY METAL EMISSIONS FROM INCINERATION OF CCA-TREATED WOODS

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INTRODUCTION

Chromium Copper Arsenate (CCA) has been used as a wood preservative since the 1970s. The production of CCA-treated woods has increased approximately 12 fold from 1970 to 1996.¹ By 1996, 79% of all the treated wood produced in the US, approximately 13 million cubic meters, was CCA-treated wood. Within Florida, 1 million pounds of the chemical were disposed during 1996.² Solo and Townsend¹ reported that by 2016 it would reach 6.8 million pounds. In Florida, the majority of the CCA-treated waste is processed through construction and demolition recycling facilities, resulting in a wood waste composition containing on average 6% CCA-treated wood. The primary market for wood waste is energy recovery and, therefore the majority of CCA-treated wood waste is burned for energy recovery purposes.

During combustion, the heavy metals in these woods may escape from the combustion system and can be emitted into the atmosphere. Arsenic is known to be a volatile metal and is likely to enter the gas stream by vaporization.³ Hirata *et al.*⁴ performed an isothermal pyrolysis of CCA-treated wood and reported that almost all chromium and copper from the CCA woods were recovered from the ash while the majority of arsenic evolved into the gas phase. Once the metallic vapors exit the high temperature region and enter the low temperature region downstream, they may form submicrometer-sized aerosols.⁵ Unfortunately, conventional air pollution control devices such as electrostatic precipitators (ESPs) have their minimum collection efficiencies at the submicrometer range.^{6,7}

After combustion, the heavy metals are concentrated in the remaining ash.¹ The concentration of arsenic, chromium, and copper in the ash ranged from 8980–45000 mg/kg, 1780–22500 mg/kg, and 2720–31500 mg/kg, respectively.¹ Pohlandt *et al.*⁹ conducted distilled water extraction on furnace, boiler, and fly ash produced from the combustion of CCA-treated wood. They reported that furnace ash produced the highest chromium concentrations (greater than 1,000 mg/L) and the fly ash produced the highest arsenic concentrations. Messick *et al.*¹⁰ performed TCLP and SPLP on the ash obtained from the combustion of various retention levels of CCA-treated wood. The TCLP limits were exceeded for arsenic in almost all of their CCA ash samples. Half of their CCA ash results exceeded the TCLP limit for chromium. Once a waste is regulated as hazardous it must be disposed differently from regular wastes, which eventually increases the cost, the paperwork, and the labor needed for their disposal.

To prevent these undesirable consequences, a new technique needs to be developed. Using mineral sorbent materials to control heavy metals has been studied by a number of researchers since the late 1980s.^{3, 11–13} Uberoi and Shadman¹¹ and Ho *et al.*¹² used silica, alumina and various naturally available materials (*i.e.*, bauxite, kaolinite and lime) to capture lead and cadmium. Mahuli *et al.*³ demonstrated that calcium hydroxide can effectively capture volatile gaseous arsenic and confirmed the presence of calcium arsenate in the ash. Gullett and Ragnunathan¹³ observed the reduction in submicrometer concentrations of arsenic when hydrated lime and limestone were injected into the combustion system. Chen and Wey¹⁴ studied the effects of various operating conditions, such as the presence of organic chloride (PVC), inorganic chloride (NaCl), and sodium sulfide (Na₂S), on the capacity of a sorbent (limestone) to capture the heavy metals during combustion. The experiences of these researchers suggest that sorbent technology can be applied to the incineration of CCA-treated wood. The common mineral sorbents will potentially react with the heavy metals within the CCA-treated wood and also may impact the leaching behavior of these metals.

The objective of this research is to control both the emissions and leaching of heavy metals from the incineration of CCA-treated woods by using sorbent materials. Equilibrium calculations were performed to identify potential materials that can effectively bind those metals. Experiments were conducted to study their performance. The information obtained in this study will result in a better management option for CCA-treated wood disposal.

EQUILIBRIUM MODELING

In a high temperature system, reactions are generally very fast, and equilibrium conditions are possibly achieved. Hence, thermodynamic equilibrium calculations can be used to predict the behavior of a high temperature system. In this study, thermodynamic equilibrium calculations were performed to identify the sorbent materials which can potentially react with the heavy metals in the CCA-treated wood. The effects of sulfur and chlorine, on the formation of sorbent-metal compounds were also analyzed. Available thermochemical data were gathered^{15, 16} and the data of any relevant reactants and possible products were included in the calculations. The calculations were performed using the software STANJAN.¹⁷ The calculations were performed assuming 100% excess air for a wide temperature range. The simulation conditions are listed in Table 1.

Table 1. Simulation conditions in each calculation.

Calculation # or Figure #	Type of Sorbent Tested	Moles of Species Included in Calculation					
		Metal	NaHCO ₃	Sorbent	MgO	S	Cl
1	Na	1	2	N/A	N/A	0	0
2		1	2	N/A	N/A	0	10
3		1	2	N/A	N/A	10	0
4		1	N/A	N/A	0.5	0	0
5	Mg	1	N/A	N/A	0.5	0	10
6		1	N/A	N/A	0.5	10	0
7	Na, Mg, K	1	2	2	0.5	0	0
8		1	2	2	0.5	10	10

Chromium-Sorbent System

Calculations were first performed for chromium. Figure 1 shows the result of using a Na-based sorbent. As shown, sodium chromate (Na_2CrO_4) is the thermodynamically most stable

Figure 1. Effectiveness of Sodium Sorbent on Chromium Capture

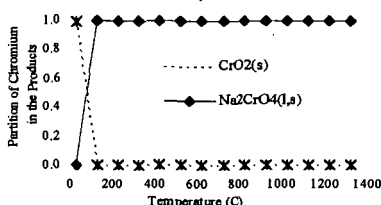
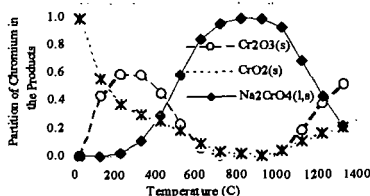


Figure 2. Effect of Chlorine on Sodium Sorbent



compound among other possible chromium compounds. The result indicates the potential use of Na-based sorbents. Chlorine and sulfur are known to have strong affinity to react with many metals and hence their impact on the sorbent's performance is investigated. As shown in Figure 2, when chlorine is present in the system, chlorine consumes all the sodium available for chromium and forms sodium chloride (NaCl) at temperatures below 500°C and above 1200°C. Between 500°C and 1200°C, hydrochloric acid is more thermodynamically stable than NaCl ; therefore, Na becomes available for chromium to form Na_2CrO_4 . Thus, the Na-base sorbent is effective only at that temperature range. Figure 3 shows the effect of sulfur. As shown, when sulfur is present in the system, chromium sulfate is the major chromium species up to around 550 °C. Above this temperature, Cr_2O_3 becomes the dominant chromium species. Sodium is in the form of Na_2SO_4 only above 1000°C when the sodium sorbent becomes effective.

Figure 3. Effect of Sulfur on Sodium Sorbent

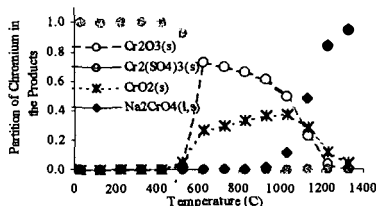


Figure 4. Effectiveness of Magnesium Sorbent on Chromium Capture

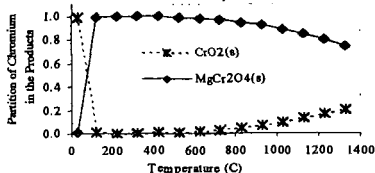
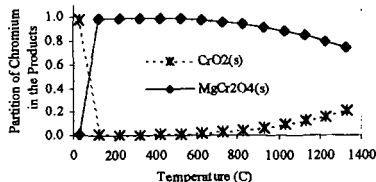


Figure 5. Effect of Chlorine on Magnesium Sorbent



for a Mg-based sorbent is shown in Figure 4. As shown, magnesium can also form stable compounds with chromium at a wide temperature range, and magnesium chromite (MgCr_2O_4) is the predominant chromium species. The effects of chlorine and sulfur on the Mg-based sorbent were also investigated. Figure 5 shows the effect of chlorine on the Mg-based sorbent. As shown, MgCr_2O_4 still remains to be the most stable chromium compound in the system even when a significant amount of chlorine is present. Magnesium has stronger affinity to react with chromium than chlorine does. On the other hand, when a significant amount of sulfur is present in the system, magnesium is consumed by sulfur and forms magnesium sulfate MgSO_4 . This trend continues up until around 700 °C, above which magnesium sulfate becomes unstable and the Mg becomes available for chromium to form MgCr_2O_4 .

Arsenic-Sorbent and Copper-Sorbent Systems

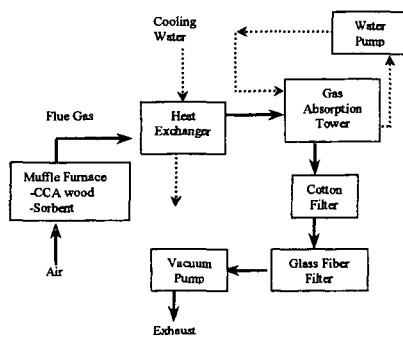
Calculations were also performed for arsenic and have been reported by Barton and Wu.¹⁸ In short, alkali metals and alkaline earth metals are effective though the performance may be reduced when chlorine or sulfur is present in the system. In addition, aluminum is also effective to capture arsenic. Calculations were not performed for copper due to the lack of thermochemical data for potential compounds between candidate sorbents and copper.

Considering all the modeling results for arsenic and chromium capture, alumina Al_2O_3 , lime $\text{Ca}(\text{OH})_2$, and soda ash Na_2CO_3 were chosen to be used in the combustion experiments.

EXPERIMENT

The experimental set-up is shown in Figure 6. CCA wood is combusted in a fluidized bed combustor inside the muffle furnace. The hot flue gas is directed into the heat exchanger designed to condense organic matter. The gas stream exiting the heat exchanger enters two columns of absorption spray towers. Each tower is 4 inches in diameter and 2.5 feet in height. The diameter of the column was small enough to achieve good contact between the gas stream and the spraying water without the use of packing materials. Tap water was constantly sprayed from the top of the column and was recirculated until each combustion run finished. The gas streams are further carried into a column of cotton filter to capture the remaining moisture content, volatile matter, and particulate matter in the gas stream. A glass fiber filter was used as the final particulate control device to capture the remaining micron-sized particulate matter. The flow of the gas stream was drawn by a vacuum pump at a flow rate of 30 lpm.

Figure 6: Schematic of Entire Set-Up



The type of CCA-treated wood combusted was type-C with 2.5 pcf (2.5 lb of chromium copper arsenate per ft³ of dry wood). The wood was processed into sawdust, which was combusted with three different sorbents within a fluidized bed consisting of two layers of stainless steel meshes. 100 g of CCA wood was thoroughly mixed with 18 g of the selected sorbent and placed on the lower stainless steel mesh. Combustion products collected in this layer correspond to the bottom ash in general incineration systems. Another 18 g of sorbent was evenly spread on the upper steel mesh. This layer is designed to capture any vaporizing gaseous metals from the burning of CCA wood in the lower layer. Metals collected in this layer correspond to those observed in the fly ash in general incineration systems. Two sets of experiments were conducted. The experimental conditions are listed in Table 2 below. In the first set, only CCA-treated wood is combusted at three temperatures to establish the baseline. In the second set, three sorbent materials representing different groups (alkali metal, alkaline earth metal, and aluminum-based sorbents) are added to the system to investigate their performance in capturing the metals. After each combustion run, the leaching behavior and the total mass of the metals from the ash is analyzed, according to EPA Method 1311, Toxicity Characteristic Leaching Procedure. Total mass of each of these metals in the ash was analyzed according to EPA Method 3050B, Acid Digestion of Sediments, Sludges, and Soils. Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy. The total mass of these metals in the original CCA sawdust was also analyzed by Method 3050B. Identification of the compounds in the obtained ash is done by X-ray Diffraction (XRD).

Table 2. Experimental Conditions

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	Temperature	CCA Wood	Mass of Materials added (g)			Sulfur on Bottom Layer
			Name	Bottom Layer	Top Layer	
Set I	600 °C	100g	None	N/A	N/A	0 g
	750 °C					
	900 °C					
Set II	600 °C	100g	Al ₂ O ₃	18g	18g	0g
			Ca(OH) ₂	18g	18g	
			Na ₂ CO ₃	18g	18g	
	750 °C		Al ₂ O ₃	18g	18g	
			Ca(OH) ₂	18g	18g	
			Na ₂ CO ₃	18g	18g	
	900 °C		Al ₂ O ₃	18g	18g	
			Ca(OH) ₂	18g	18g	
			Na ₂ CO ₃	18g	18g	

RESULTS AND DISCUSSIONS

In our preliminary study, four experiments have been conducted at 750°C. For the first run, 100 g of CCA wood was burnt without any sorbent. For the other three runs, 12 g of Al_2O_3 , $\text{Ca}(\text{OH})_2$, and NaHCO_3 were individually mixed with 100 g of CCA wood. It took two hours to reach 750°C which was then maintained for 45 minutes. After combustion the obtained ash was analyzed for the leaching behavior of heavy metals and the composition identified. The leaching levels from the TCLP tests are shown in Table 3 and the results from X-ray diffraction for NaHCO_3 are given in Figures 7 and 8 (other results are not shown due to space limit).

Table 3: TCLP results for CCA Wood Combustion with and without the Addition of Sorbents.

	As (mg/L)	Cr (mg/L)	Cu (mg/L)	pH (raw)	PH (TCLP)
CCA-Only	87.0	16.9	23.2	6.3	2.9
CCA + Al_2O_3	7.9	19.0	33.0	6.9	2.7
CCA + $\text{Ca}(\text{OH})_2$	0.8	84.3	1.0	12.5	11.5
CCA + NaHCO_3	3687.0	4627.0	2.1	12.6	12

The TCLP criteria for arsenic and chromium are 5 mg/L. Unfortunately, none of the ash samples passed the TCLP criteria. However, when alumina was added the arsenic leaching was 11 times lower than that without any sorbent (CCA-Only). The calcium based sorbent appears even better. The arsenic concentration drastically decreases to 0.8 mg/L, 110 times lower than the CCA-Only case. Speciation plays an important role here as the solubility varies with speciation. The potential arsenic-sorbent products ($\text{Ca}_3(\text{AsO}_4)_2$ and AlAsO_4) are insoluble.¹⁹ This explains the reduced leaching level observed. Unfortunately, these species were not identified in the XRD.

It is generally known that the pH of the leachate has strong impact on the leaching behavior of heavy metals.²⁰⁻²¹ Warner and Solomon²² found that copper, chromium, and arsenic were found in the leachate of both new and weathered CCA-treated jack pine, with significantly higher levels of all metals at lower pH values. One interesting phenomenon observed in our results regards this low pH effect on arsenic leaching. Although the pH of the solution after a TCLP test was low (< 3) for both CCA-Only and CCA + Al_2O_3 , the addition of alumina reduced the leaching of arsenic by 11 times. This comparison proves that addition of alumina reduces the arsenic leaching under aggressive conditions. Dutre and Vandecasteele²³ have observed and also calculated that the addition of lime into a waste fly ash decreases the leaching level of arsenic. However, it is important to emphasize here the distinct difference between the addition of lime before and after the combustion. Lime captures volatile metals during the combustion, which not only reduces the leaching but also reduces the air emission of toxic metals.

Figure 7 X-ray diffractograms of CCA+ Na_2CO_3 Bottom Ash

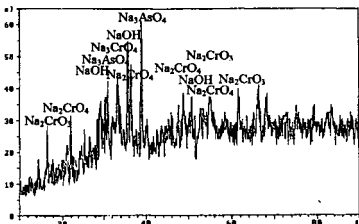
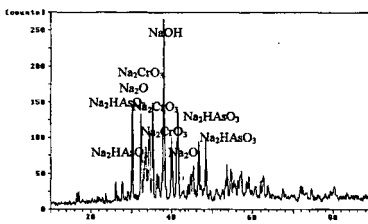


Figure 8 X-ray diffractograms of CCA+ Na_2CO_3 Fly Ash



Unfortunately, neither alumina nor lime reduced the leaching of chromium. The cause of this poor result is not clear at this stage. XRD results show that chromium oxide instead of calcium chromite or aluminum chromate is the identifiable component. The result indicates that the sorbent materials are not effective in reacting with the chromium in the system. Mass transfer or reaction kinetics may be the limiting factor.

Leaching of copper was reduced by the addition of lime and sodium bicarbonate. Several studies have shown that copper is known to leach more at low pH.^{24,25} The raised pH of the leachate solution most likely caused this low leaching level of copper.

The addition of sodium sorbent such as sodium bicarbonate, on the other hand, caused an incredible amount of leaching. This is due to the formation of very soluble compounds such as Na_3AsO_4 and Na_2CrO_4 identified by the XRD (Figures 7 and 8). As far as the leaching is concerned, this result is highly undesirable. However, this result can be interpreted in another way. Using these leaching levels of arsenic and chromium, a mass balance calculation was performed to obtain how much of the original amount of these metals in 100 g of wood was still present in the ash. It was found out that at least 78% of arsenic and 88% of chromium still remains in the ash after the combustion. These are very conservative values since these are derived only from a leaching test, not the total metal analysis with an aggressive acid digestion. Typically, only 20–30% of arsenic is reported to stay in the bottom ash. Hence, Na-based sorbent is very effective in retaining arsenic in the bottom ash.

CONCLUSIONS

CCA-treated wood contains a chemical preservative that consists of arsenic, chromium and copper. The majority of the recycled CCA-treated wood waste is currently burned for energy recovery purposes. There are two major problems associated with the combustion of CCA-treated wood: the emission of heavy metals as gaseous or particulate matter and the leaching of these metals from the ash. Application of sorbent technology may solve these two problems simultaneously.

Thermodynamic equilibrium calculations were performed to predict potential sorbent materials for chemically adsorbing the heavy metals in the CCA-treated wood. The results suggest that alumina, alkaline earth metals and alkali metals are effective for capturing both arsenic and chromium. However, alkali metal-based sorbents become less effective when sulfur and chlorine are present in the combustion system. According to these modeling results, alumina, lime and sodium bicarbonate were selected and their performance was examined in an experimental combustion system. The CCA wood sawdust was combusted with three different sorbents within a fluidized bed. TCLP tests were performed on the obtained ash to test the leaching behavior of heavy metals. XRD was performed on the ash sample to identify the products. The addition of alumina and lime greatly reduced the arsenic leaching. None of the sorbents reduced the leaching of chromium. The cause of this poor result is not clear at this stage. Leaching of copper was low when lime or sodium bicarbonate was added as sorbents. This is probably due to the high pH caused by lime and sodium bicarbonate in the leachate. The addition of the sodium sorbent caused an incredibly high leaching level of arsenic and chromium. It was found out that approximately 78% of arsenic and 88% of chromium still remains in the ash after the combustion, showing the sodium sorbent is very effective in retaining arsenic in the ash, which prevents the emission of arsenic.

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